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SPOT TEST DETECTION AND COLORIMETRIC DETERMINATION OF ANILINE, NAPHTHYLAMINE AND ANTHRAMINE DERIVATIVES WITH 4-AZOBENZENEDIAZONIUM FLUOBORATE

Eugene Sawicki, et al

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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Eugene Sawicki, James L. Noe and Francis T. Fox
Laboratory of Engineering and Physical Sciences
Division of Air Pollution
Robert A. Taft Sanitary Engineering Center
Public Health Service
U. S. Department of Health, Education and Welfare
Cincinnati 26, Ohio

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SPOT TEST DETECTION AND COLORIMETRIC DETERMINATION OF ANILINE, NAPHTHYLAMINE AND ANTHRANILE DERIVATIVES WITH 4-AZOBENZENEDIAZONIUM FLUOBORATE

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SUMMARY

Some new sensitive procedures are introduced for the detection and determination of aniline, α- and β-naphthylamines, and α- and β-anthramines, as well as their N-alkyl and N,N-dialkyl derivatives. The chromogens are (p-phenylazophenylazo) - aniline, -naphthylamine and -anthramine dyes. For example with N,N-dimethylaniline, the blue dication of N,N-dimethyl-p-(p-phenylazophenylazo) aniline is formed. The absorptivity of this chromogen (i.e. the pure dye or the dye obtained in the colorimetric procedure) is 0.82 μg^{-1} ml cm^{-1}. In the analysis for N,N-dimethylaniline Beer's Law was obeyed from 0.1 to at least 3.6 µg per ml of final solution. Because of the widely differing rates of reaction naphthylamine or anthramine derivatives can be determined in the presence of aniline derivatives. Also, with the help of a masking agent a dialkylaniline can be determined in the presence of primary and secondary amines. Spot tests for aniline, naphthylamine and anthramine derivatives are described, but their sensitivity does not compare with the sensitivities obtained in the colorimetric procedure.

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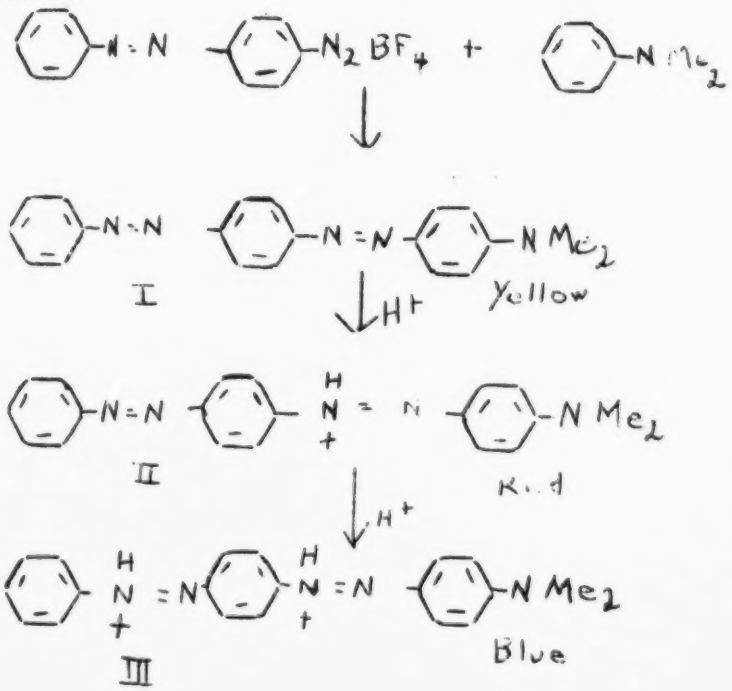
INTRODUCTION

As a result of our expanding industrialization various types of aniline derivatives have been introduced into the human environment. Many of these compounds have been shown to have toxic properties; threshold limits for aniline, N,N-dimethylaniline and o-toluidine have been placed at 5 ppm.[1] Consequently, it was desirable to develop methods of analysis for aniline derivatives. Colorimetric procedures for aniline[2-4] and for polycyclic aromatic primary amines[4] are available in the literature. Several methods for the determination of aniline and N,N-dimethylaniline in the air have been described.[5,6] Although these methods are fairly sensitive, they were never thoroughly evaluated, and are less sensitive and more complicated than the 4-azobenzenediazonium fluoborate procedure.

The use of diazotization in the determination of aromatic amines has been known for a long time.[7] The method involves the reaction of a diazotized aromatic amine with an aromatic amine coupling agent. In the determination of sulfanilamide through diazotization and coupling with N-1-naphthylethylenediamine, the final chromogen absorbs at 545 mμ with a molar absorptivity of 51,500.[8] The chromogen obtained in the colorimetric determination of N-phenyl-1-naphthylamine with p-nitrobenzenediazonium chloride absorbs at 555 mμ with a molar absorptivity of 37,000.[9]

In this paper a new and more sensitive diazotization method for the determination of several types of aromatic amines is introduced. Some simple spot tests are also described.

The mechanism of the reaction as applied to N,N-dimethylaniline is as follows:



The compound is analyzed at the blue stage because of the more intense color of the dication as compared to the monocation. 10

In a solvent containing 30 ml of 2-methoxyethanol diluted to 100 ml with concentrated hydrochloric acid the pure dye absorbed at 632 mμ as did the solution obtained in the colorimetric determination of N,N-dimethylaniline. At this wavelength maximum the latter solution had a molar absorptivity of 100,000 as compared to 100,000 obtained for the pure dye. These results indicate that a 100% yield of chromogen is obtained in the determination of N,N-dimethylaniline.

EXPERIMENTAL

Reagents and Equipment. 4-Azobenzenediazonium fluoborate was prepared from 4-aminoazobenzene.[4] A solution of 0.1% of 4-azobenzenediazonium fluoborate in 2-methoxyethanol was used as the reagent in the analytical work. All organic nitrogen compounds were obtained from commercial sources and were purified by crystallization to a constant melting point or by distillation.

A Cary Model 11 recording spectrophotometer with 1 cm cells was used in the colorimetric determination of aniline derivatives.

Microtube Procedure. To a drop of the 2-methoxyethanol test solution was added 2 drops of 0.1% 4-azobenzenediazonium fluoborate. The tube was then heated in a boiling water bath for 6 minutes. Then 2 drops of concentrated hydrochloric acid was added. Because of the reagent's interfering yellow color at low concentrations of test compound, a blank is advisable in doubtful cases. Colors and limits of identification are given in Table I.

Spot Paper Procedure. To one drop of the 2-methoxyethanol test solution spotted on paper was added 2 drops of 0.1% 4-azobenzenediazonium fluoborate. The spot was treated with a jet of steam for 30 seconds and then with a jet of hydrogen chloride gas. Instead of the gas, a drop of concentrated hydrochloric may be placed on the paper. However, the sensitivities are lower in the latter procedure because of diffusion. Colors and limits of identification are given in Table I.

Colorimetric Procedure. To 5 ml of the 2-methoxyethanol test solution in a 50 ml volumetric flask was added 10 ml of 0.1% 4-azobenzene diazonium fluoborate. The mixture was heated for 6 minutes in a boiling water bath. It was cooled with an ice water bath and then diluted to the mark with concentrated hydrochloric acid while cooling to room temperature. The absorption spectrum

was then immediately determined. The wavelength maxima and molar absorptivities obtained for different aniline derivatives are given in Table I.

DISCUSSION OF QUALITATIVE TESTS

Two modifications of the spot test procedure are introduced in this paper. A blank must be run in conjuction with the test, especially in the microtube method, at concentrations near the identification limit. This is because the blank has a deep yellow color and the presence of a small amount of blue chromogen would then give the test solution a yellow green color. This interference could cause difficulty. α-Anthramine is characterized by the fact that it gives a blue color in the microtube method without any hydrochloric acid. Neither the aniline nor naphthylamine derivatives do this.

DISCUSSION OF COLORIMETRIC PROCEDURE

The method introduced in this paper for the determination of N,N-dimethylaniline has a very high sensitivity potential for colorimetric analysis.

Other N-alkyl and N,N-dialkyl anilines give colors of differing intensity. This variation in intensity is mainly due to the varying yields of bisazo dyes obtained in the colorimetric procedure. A slower rate of reaction could have a drastic effect on the yield. In many cases the presence of an orange to red dicationic tautomer (involving salt formation at an azo nitrogen and the amino nitrogen) also helps to decrease the intensity of the blue color of the bisazo dye dication.[10]

Of the aromatic amines investigated, the ring-substituted aniline derivatives, N,N-dimethyl-α-naphthylamine and β-naphthylamine gave the lowest intensities. m-Toluidine and N,N-dimethyl-m-toluidine gave the highest relative intensities, due mainly to the electron donor effect of the m-methyl group of the toluidine in the final azo dye.

While aniline derivatives only reacted readily with the reagent at the boiling point of water, the naphthylamines and anthramines reacted at room temperature (Table I). After the reaction of anthramine and reagent at room temperature, dilution with 2-methoxyethanol to 50 ml gave a purple solution absorbing at 566 mμ with a molar absorptivity of 28,000. These diverse reactions at room temperature and at the boiling point of water should be of value in characterizing some of the amines.

The colorimetric procedure has been developed so as to give optimum results with N,N-dimethylaniline; in this case a 100% yield of the bisazo dye dication, III, was obtained. With proper modification of the standard colorimetric procedure more intense colors could probably also be obtained for the other aromatic amines. This improvement with modification of conditions has been shown for the α-naphthylamines.

The following variations in the standard colorimetric procedure for N,N-dimethylaniline are of interest. Optimum results were obtained with 0.1 to approximately 0.3% of the reagent (Figure I). However, the blank was fairly dark, so 0.1% concentration was chosen as giving the best all-around results. When the reagent and the N,N-dimethylaniline test solution were heated in a boiling water bath, it took 6 minutes of heating to obtain the maximum intensity (Figure 2). Shorter periods of heat had a drastic effect on the intensity; longer periods had a slight effect. The stability of the color was also investigated (Figure 3). The absorbance decreased gradually at a steady rate. Readings were preferably taken on a fresh solution, or at least, within a few minutes after the acid was added. The color obtained in the determination of N,N-dimethylaniline was found to obey Beer's Law from 5 to at least 180 μg per 50 ml of final solution.

DECREASED REACTIVITY DUE TO SUBSTITUENTS

Some aniline derivatives gave a very weak to negligible color in the standard colorimetric procedure. In compounds such as the nitroanilines, o-chloroaniline, N,N-dimethyl-m-aminobenzoic acid, N,N-dimethyl-p-bromaniline, N,N-dimethyl-p-aminobenzaldehyde, the N,N-dimethyl nitroanilines and N,N-dimethyl-p-toluidine. The presence of an electronegative group or a group para to the amino group had an adverse effect on the activity. In N,N-dimethyl-o-toluidine the low order of reactivity is due to the strong steric effect of the o-methyl group.[11] This effect forces the dimethylamino group out of the plane of the molecule and as a result causes a low yield of the bisazo dye dication.

Interferences. A few diphenylamines and heterocyclic imines were tested by the standard colorimetric procedure. N-Methyl-diphenylamine and diphenylamine gave bands at 640 mμ with molar absorptivities of approximately 13,000 and 17,000, respectively. Indole and carbazole gave bands at 560 and 605 mμ with molar absorptivities of 11,000 and 6,000, respectively. Because of their relatively weak basicity, diphenylamines, indoles and carbazoles can be readily separated from the more basic aromatic amines. In this way aniline derivatives could be determined in the presence of these compounds.

Phenols could be expected to react with the reagent. Phenol itself gave an orange solution in the standard colorimetric procedure which had negligible absorption near 600 mμ. α-Naphthol gave a band at 625 mμ with a molar absorptivity of 7,000. If necessary, phenols could be separated by alkaline extraction.

2,4-Pentadione reacted in the standard colorimetric solution gave a red solution with a band at 535 mμ and a molar absorptivity of 21,000.

Nitromethane, dibutylamine, isobutylamine, formaldehyde and acetone gave negative results.

Acetic anhydride tended to inhibit color formation.

Determination of α-Naphthylamine in a Mixture. Reaction of aniline derivatives with the reagent at room temperature was extremely slow. A negligible reaction was observed with N,N-dimethylaniline after 10 minutes of standing. Because of the wide difference in the rate of reaction of aniline derivatives (as opposed to naphthylamine and anthramine derivatives) with the reagent at room temperature, a naphthylamine or anthramine could be determined in the presence of aniline derivatives.

As an example of this phenomenon, a liquid mixture was prepared consisting of 71.5 μg of α-naphthylamine, 930 μg of aniline, 1070 μg of N-methylaniline, and 1210 μg of N,N-dimethylaniline. Reaction of this mixture in the standard colorimetric procedure (modified by substitution of 10 minutes of standing at room temperature for 6 minutes of heating on the water bath) gave an absorption spectrum with maxima at 500 and 642 mμ. The band with a peak at 642 mμ had an absorbance of 0.96. The band with a peak at 500 mμ was mainly derived from aniline and N-methylaniline and apparently had little effect on the intensity of the long wavelength band, for 71.5 μg of α-naphthylamine reacted in the same procedure gave a band at 642 mμ with an absorbance of 0.95. The absorbance thus obtained in the mixture corresponds to 70.8 μg of α-naphthylamine which is in excellent agreement with the amount of α-naphthylamine calculated to be present.

DETERMINATION OF N,N-DIMETHYLANILINE IN A MIXTURE

For the determination of N,N-dimethylaniline in the presence of primary and secondary amines, the use of acetic anhydride as a masking agent was tried. A mixture of 12.1 μg of N,N-dimethylaniline and 2 μl of acetic anhydride were heated 10 minutes, cooled and reacted by the standard colorimetric procedure. A molar absorptivity of 73,000 was obtained; without the acetic anhydride the molar absorptivity was 85,000. When a mixture of 12.1 μg of N,N-dimethylaniline

and 14.3 μg of α-naphthylamine was similarly analyzed, a molar absorptivity of 75,000 was obtained for N,N-dimethylaniline, essentially a 96% recovery. When a mixture of 12.1 μg N,N-dimethylaniline, 14.3 μg of α-naphthylamine, 10.7 μg of N-methyl-aniline, and 9.3 μg of aniline was analyzed by the same procedure, a molar absorptivity of 85,000, or a 113% recovery of N,N-dimethylaniline, was obtained. These results show that the determination of a tertiary amine in the presence of primary and secondary amines with the help of an acylating masking agent is worthy of further investigation.

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LIST OF FIGURES

Fig. 1. Effect of concentration of azobenzenediazonium fluoborate in the reagent solution on the absorbance obtained in the standard colorimetric procedure with N,N-dimethylaniline (2×10^{-5} M) at λ max. 632 mμ.

Fig. 2. The effect on the absorbance at λ max 632 mμ of the heating time at 100° of the reagent and N,N-dimethylaniline in the colorimetric procedure. Final concentrations of N,N-dimethylaniline - 2×10^{-5} M.

Fig. 3. Change of absorbance with time at λ max 632 mμ of the final solution obtained with N,N-dimethylaniline (2×10^{-5} M) in the standard colorimetric procedure.

TABLE I. COLORIMETRIC AND SPOT TEST DATA OBTAINED IN THE ANALYSIS FOR PHENYL-, NAPHTHYL- AND ANTHRYL-AMINES WITH 4-AZOBENZENEDIAZONIUM FLUOBORATE

Compounds	Colorimetric		Spot Tests, Ident. Limit, μg			
	λ max. mμ	$\epsilon \times 10^{-3}$	Color[a]	Microtube	Color	Paper
Aniline	610	8	V	7	V	7
o-Methylthioaniline	610	9	B	9	B	9
o-Toluidine	618	23	V	15	V	4
o-Anisidine	626	48	V	9	V	2
m-Toluidine	612	63	R	4	B	2
N-Methylaniline	623	65	V	8	V	8
N-Ethylaniline	623	73	B	9	B	9
N-n-Propylaniline	623	85	RV	10	V	17
N,N-Dimethylaniline	632	100	B	1	B	17
N,Methyl-N-ethylaniline	633	80	B	5	B	17
N,N-Diethylaniline	635	72	B	5	B	11
N-Allyl-N-methylaniline	632	83	B	5	B	11
N-Benzyl-N-methylaniline	640	73	V	4	B	14
N,N-Di-n-propylaniline	637	82	B	6	B	13
N,N-Dimethyl-m-toluidine	630	120	B	5	B	0.6

TABLE I. cont.

Compounds	Colorimetric λ max. mμ	Colorimetric $\epsilon \times 10^{-3}$	Spot Tests, Ident. Limit, μg Color[a]	Microtube	Color	Paper
α-Naphthylamine [b]	642	95	B	1	B	0.6
N-Methyl-α-naphthylamine [b]	645	99	B	18	B	0.7
N-Ethyl-α-naphthylamine [b]	645	99	B	3	B	0.8
N-1-Naphthylethylenediamine [b]	656	100	B	3	B	0.8
N,N-Dimethyl-α-naphthylamine [b]	642	22	B	2	B	2
β-Naphthylamine [b]	603	32	B	10	B	3
α-Anthramine [b]	675	42	G[c]	14	B	2
β-Anthramine [b]	625	56	G[c]	7	V	0.9

a. B=blue; G=green; V=violet; R=red. Color of product in microtube changes to green if concentrations of amine falls below ~ 10-40 μg.

b. The standard colorimetric procedure was followed except 10 minutes of standing at room temperature was substituted for the 6 minutes of heat on the water bath. In the standard colorimetric procedure involving heat the following wavelength maxima and molar absorptivities were obtained--α-naphthylamine, 610 (41,000); β-naphthylamine, 605 (57,000); α-anthramine, 544 (28,000); and β-anthramine, 623 (44,000).

c. Color obtained without heat or acid for α-anthramine is blue and identification limit is 7 μg; for β-anthramine it is violet with identification limit of 7 μg.

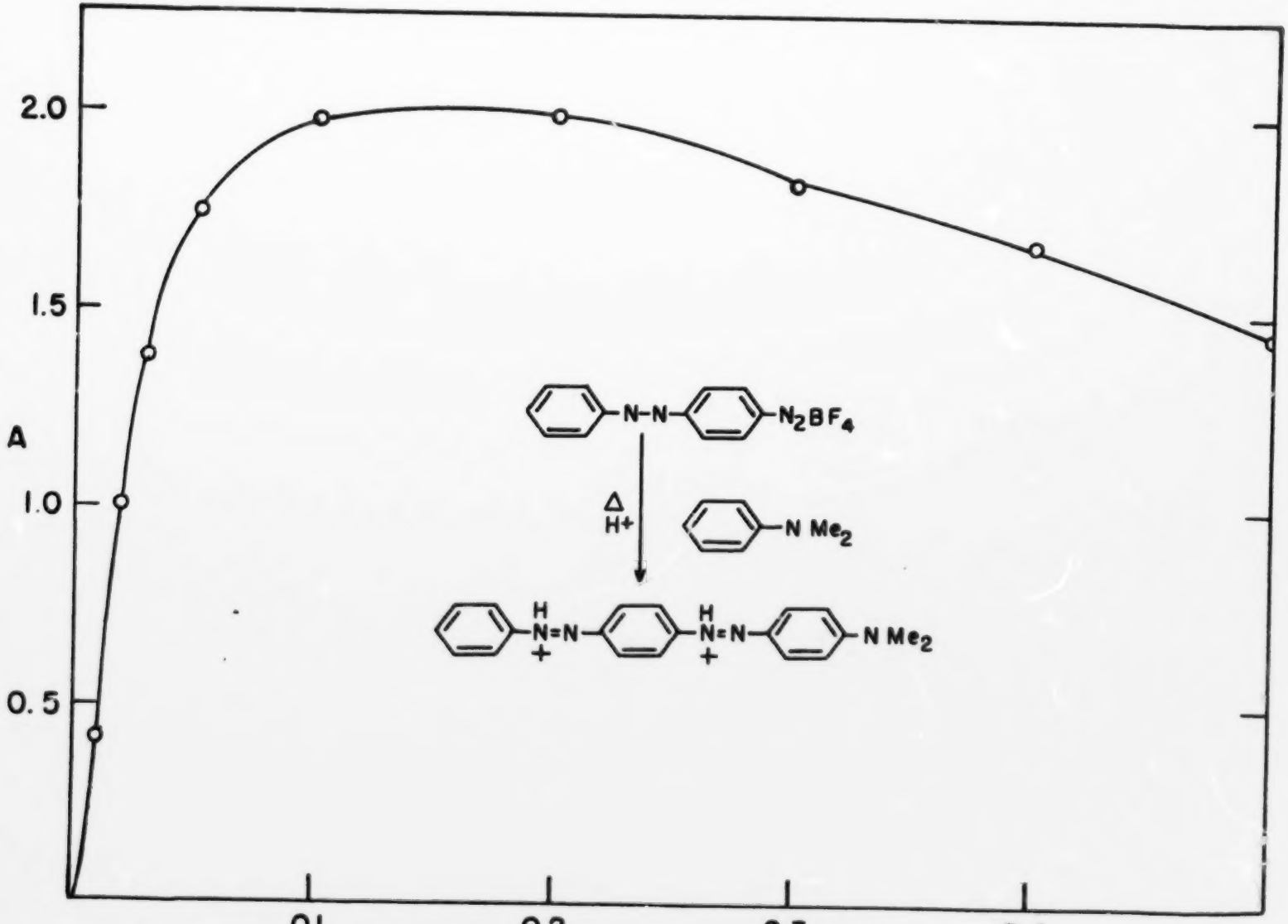
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Figure 1

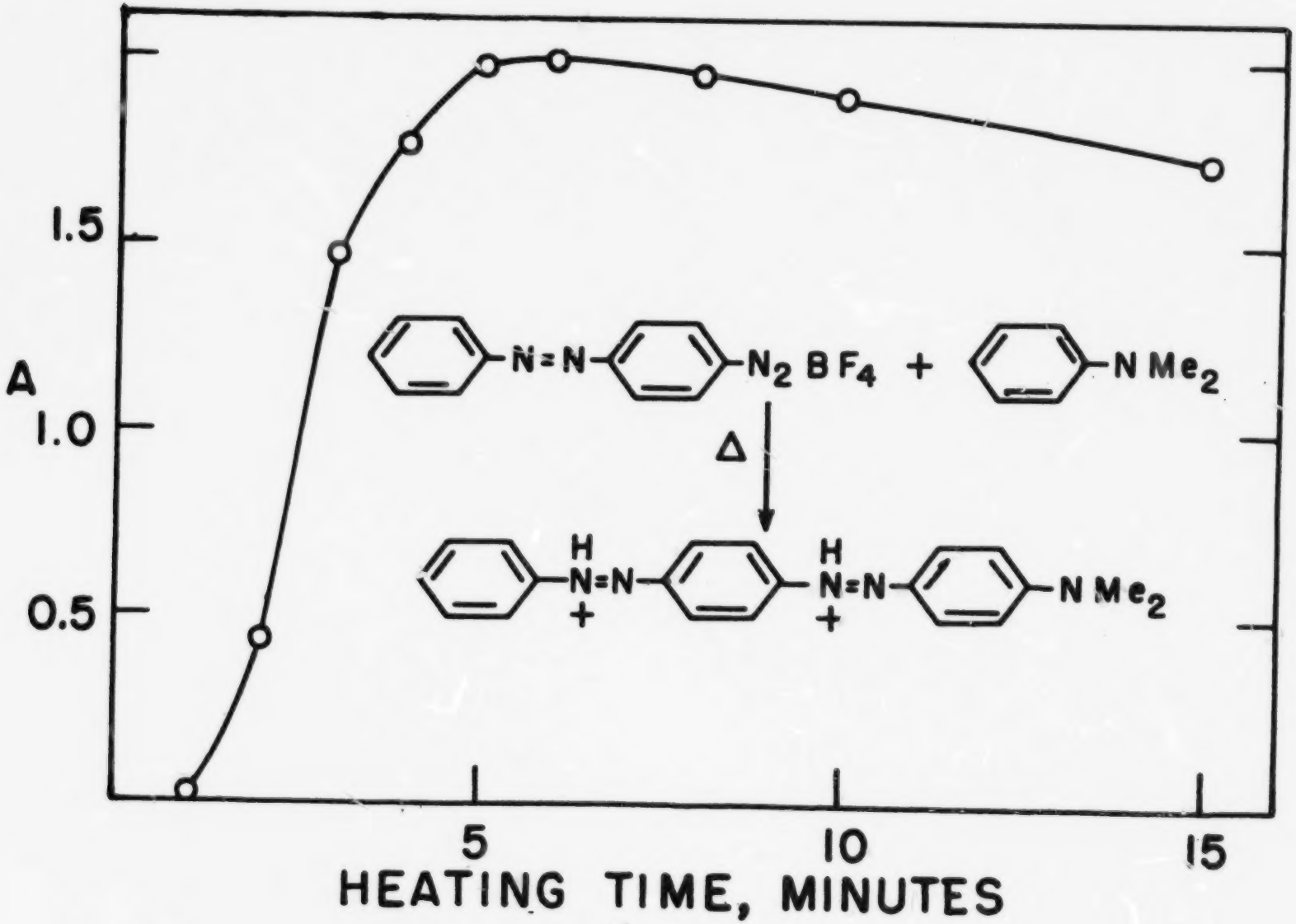


Figure 2

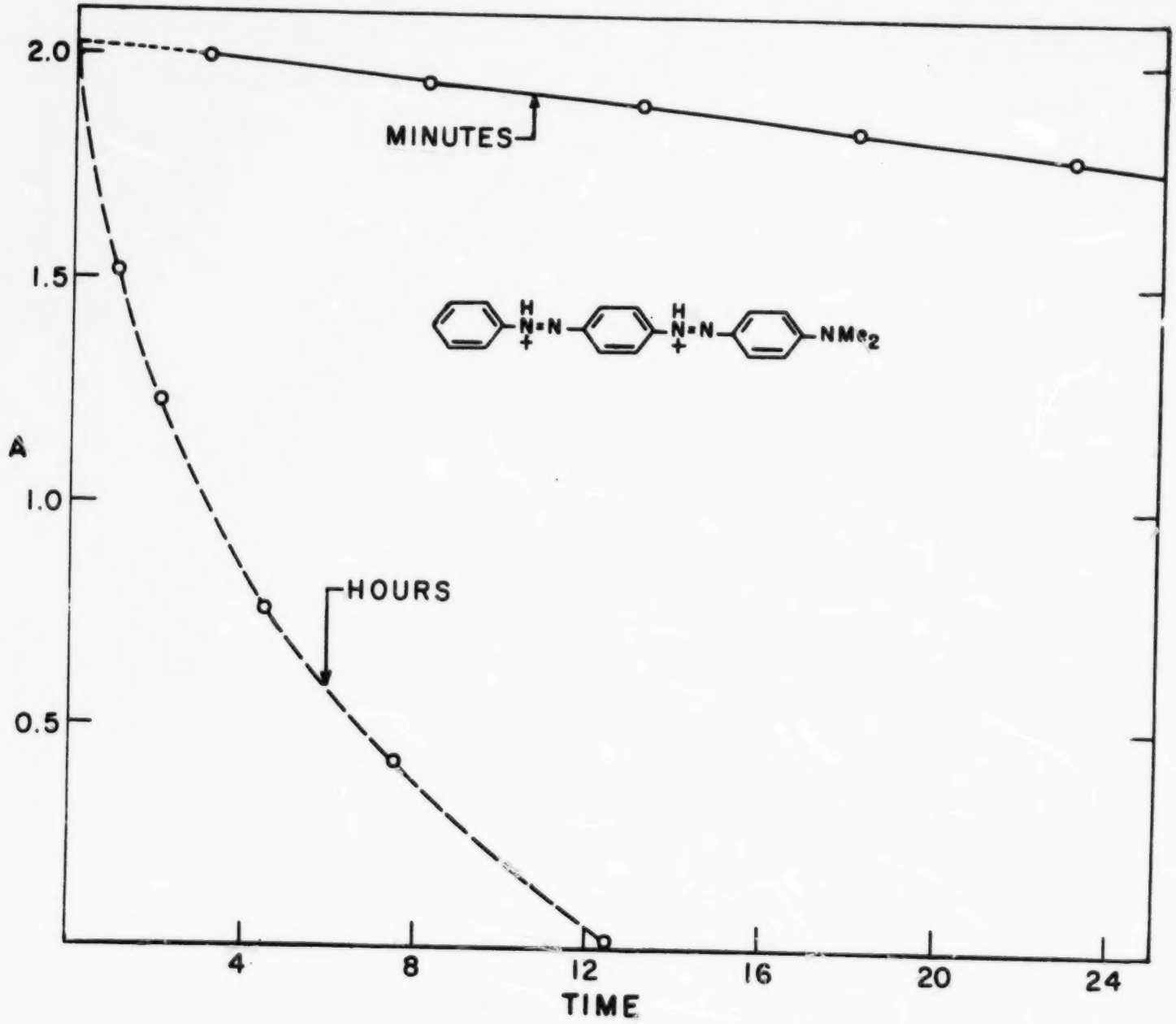
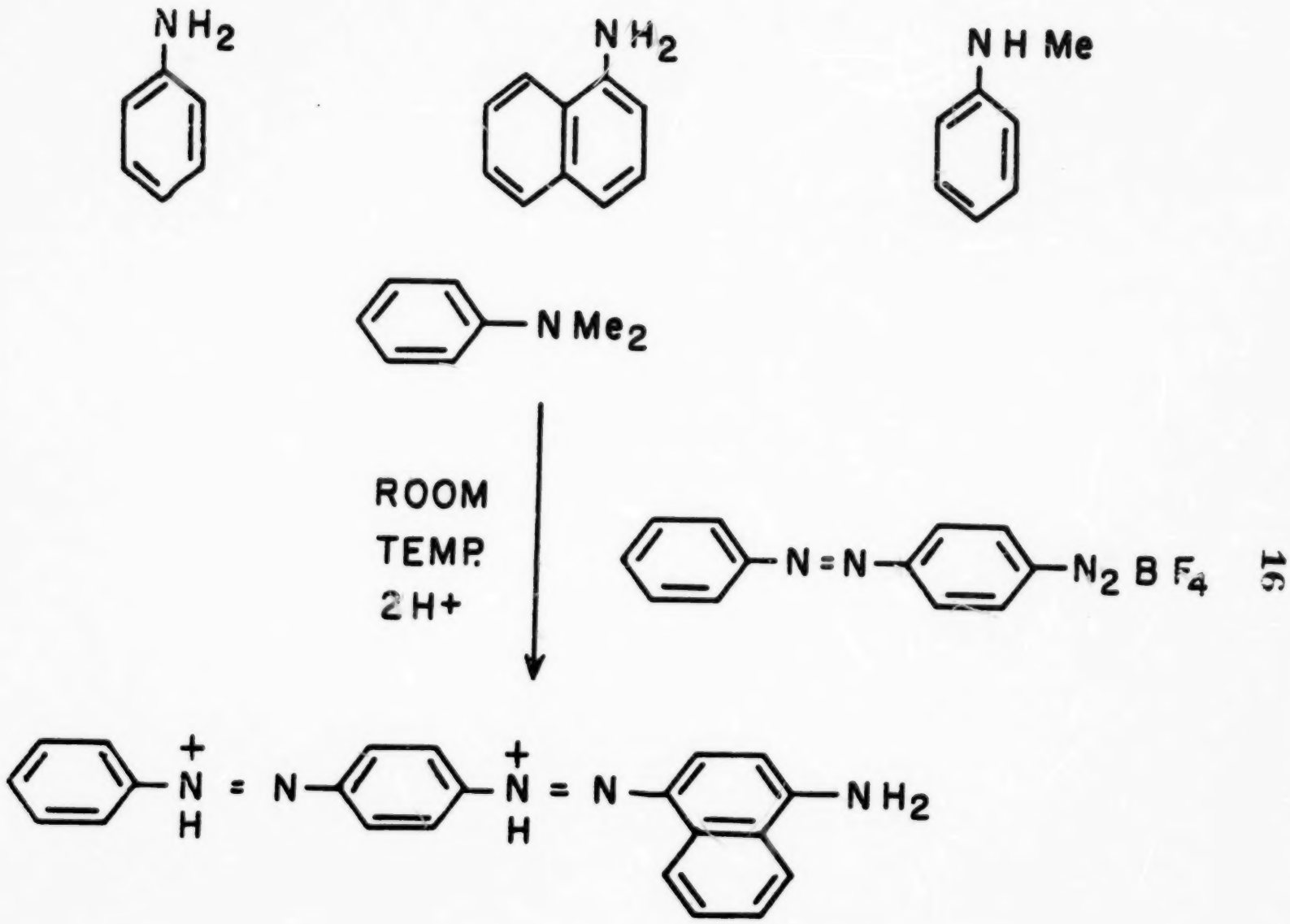


FIGURE 3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